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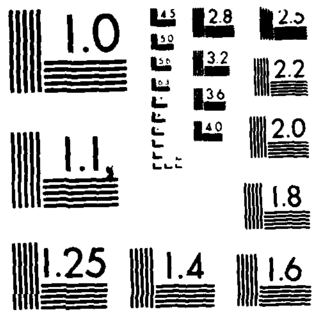

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Contract N00014-78-C-0591

Task No. NR 356-691

FINAL REPORT

Electrical Monitoring of Polymerization Reactions with the Charge-Flow Transistor

by

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May 31, 1984

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER	2. GOVT ACCESSION NO. A142267
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) Electrical Monitoring of Polymerization Reactions with the Charge-Flow Transistor - Final Report	5. TYPE OF REPORT & PERIOD COVERED Final 7/78 - 5/84
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Stephen D. Senturia	8. CONTRACT OR GRANT NUMBER(s) N-00014-78-C-0591
9. PERFORMING ORGANIZATION NAME AND ADDRESS Massachusetts Institute of Technology Cambridge MA 02139	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 356-691
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research, Code 427 800 N. Quincy Street Arlington VA 22217	12. REPORT DATE May 31, 1984
	13. NUMBER OF PAGES 7
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Microdielectrometry, dielectric cure monitoring, time-temperature-transformation diagram, epoxy resins, DGEBA, DDS, conductivity, permittivity, loss factor

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report summarizes technical activities, reports, publications, patents and student theses completed during the period of the Contract.

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Electrical Monitoring of Polymerization Reactions with the Charge-Flow Transistor

Goals

The primary goal of this program was to develop a promising new technique for the electrical monitoring of polymerizations based on a device called the charge-flow transistor, and its related device, the floating-gate charge-flow transistor. The program was directed both toward the development of the instrumentation capabilities of the device and toward the research use of the method for the study of selected polymer systems.

Background

At the start of the program in 1978, the charge-flow transistor had been reported as a possible tool for study of electrical conduction in thin polymer films. The device resembles a conventional MOSFET, but with a portion of the gate metallization replaced by the polymer film under study. Because of the relatively weak conduction in the polymer, the device turn-on time is dominated by the polymer conductivity. It was with this device that the first studies of epoxy resin cure took place, which demonstrated feasibility of using the device for serious cure monitoring studies. Based on these results, the present program was initiated.

Technical Summary

The first major effort was directed toward a quantitative understanding of the signals obtained from the charge-flow transistor during the room temperature cure of an epoxy-amine system (1). Along with this effort, a new device structure, the floating-gate charge-flow transistor was developed which was vastly simpler in terms of reproducibility and calibration. With this device, it became possible to use a wide range of ac signals for cure studies over a wide temperature range. With the use of the floating-gate charge-flow transistor, the term "Microdielectrometry" was coined as a representative name for this new measurement technology (2).

The Microdielectrometry instrumentation at this time consisted of the integrated-circuit dielectric sensor, analog instrumentation to drive the sensor with a sinusoid (frequency range 1 - 1000 Hz) and to extract response amplitude and phase from the sensor, a calculator-based controller which included the sensor calbiration in its memory, and from which the dielectric permittivity and dielectric loss factor could be obtained given the sensor amplitude and phase response (3).

This instrumentation was used to study the isothermal cure of DGEBA with m-PDA. It was found that prior to gelation, where the conductivity (hence dielectric loss factor) was relatively large, a relaxation time could be obtained from the data which was proportional to viscosity (4,5,6). Subsequent studies have shown that this relaxation time was actually due to the charging of ionic blocking layers at the electrodes (see below). A

study of DGEBA-DDS was also carried out with and without a reactive diluent (PGE) which tied up an amine functionality without producing a crosslink. Not only did the Microdielectrometer cure studies show that the addition of diluent changed the endpoint of the reaction, but post-cure ramped temperature dielectric studies could be used to extract a glass transition temperature, which decreased as expected with increasing diluent (7). The Microdielectrometer was also used to study the imidization reaction of polyimides (8).

New effort was devoted to instrumentation improvements, with several specific goals: improved calibration, incorporation and use of an in-situ temperature sensor; improved sensor packaging; and wireless telemetry capabilities. All these goals were reached to some degree. The inclusion of a diode temperature sensor was relatively staightforward, which greatly increased the ability to study ramped cures of prepregs (9,10). It also permitted a self-heated cure sensor, the "Microclave" (11,12). The improved sensor package, a novel ribbon cable package in which the active sensor electrodes are exposed to the sample but the sensitive device electronics and wire connections are covered, was completed in 1983, and represented the final critical step in making the technique practical for widespread use. In addition, new instrumentation became available which permitted the range of measurement frequencies to be extended to .005 - 10,000 Hz. This in turn made the entire measurement much more sensitive to the conductivity components of the dielectric loss (13,14). Wireless telemetry was demonstrated using a discrete-component version of the sensor transmitter (15). This has not been reduced to an integrated-circuit telemeter, however.

The new instrumentation capabilities, together with the ribbon cable package, enabled the careful isothermal study of the cure of DGEBA with DDS, and the comparison of the features of the dielectric cure response with mechanical critical points as obtained from torsional braid analysis (16). In addition, the first work on implantation of Microdielectrometer sensors into epoxy-glass and epoxy-graphite laminates was carried out to demonstrate that such experiments were feasible.

Throughout the research, ionic conductivity and its effect on the interpretation of cure data continued to pose a problem. The most recent set of experiments have been directed toward quantitatively documenting the effects of these blocking layers (17). This work, in turn, gives new insight into the results obtained with conventional parallel-plate dielectric monitoring equipment.

Perhaps the most significant result of this program has been the complete maturation of the measurement technology to the point where it is now fully accessible. In 1983, M.I.T. negotiated a license with Micromet Instruments, Inc., of Cambridge MA to make Microdielectrometry commercially available. The Naval Research Laboratory, the Army Materials and Mechanics Research Laboratory, NASA Hunstville, Westinghouse Research, and several commercial suppliers of thermosets are already using Microdielectrometry for materials research, for quality control, and for reseach in process control. In this sense, it can be said that ideas developed in the academic research laboratory have proved useful to a broader community.

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